

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 07-268250

(43)Date of publication of application : 17.10.1995

(51)Int.Cl.

C09D 5/24
C04B 14/36
C04B 16/04
C04B 28/26
C09D 1/00
C09D 1/00
C09D 1/00
C09D 1/04
C09D 5/02
C09K 15/02
// C04B111:94

(21)Application number : 06-061710

(71)Applicant : KUROSAKI REFRACT CO LTD

(22)Date of filing : 30.03.1994

(72)Inventor : MORIKAWA KATSUMI
YOSHITOMI TAKENORI
HISA HIDEYUKI

(54) CONDUCTIVE ANTIOXIDANT MATERIAL

(57)Abstract:

PURPOSE: To enable the application of a conductive antioxidant material to an electrode chuck and improve the antioxidant effects of the material at high temps. by compounding a fire-resistant aggregate, a binder, a carbon black, and a polymer emulsion.

CONSTITUTION: This material is obtd. by mixing 20-90wt.% fire-resistant aggregate, 2-30wt.% binder, 2-30wt.% carbon black, 0.05-10wt.% (solid) polymer emulsion, a graphite powder in an amt. of 20-70wt.% of the aggregate if necessary, and a water-sol. polymer in an amt. of 0.01-3wt.% of the sum of all the foregoing ingredients, adding 15-150wt.% water to the resulting mixture by pouring water from the outside, and subjecting the mixture to a homogenizing treatment. The material is applied to the side of an electrode for an arc furnace to form a dry coating film with a thickness of 100-200 μ m.

LEGAL STATUS

[Date of request for examination] 05.01.2001

[Date of sending the examiner's decision of rejection] 10.12.2002

[Kind of final disposal of application other than the examiner's decision of rejection or application]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Conductive antioxidizing material which comes to contain the fireproof aggregate, a binder, carbon black, and a polymer emulsion.

[Claim 2] Conductive antioxidizing material according to claim 1 which comes to contain graphite powder.

[Translation done.]

* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the conductive antioxidizing material which can be suitably used as conductive antioxidizing material and antioxidizing material of the graphite electrode used at the furnace using the arc of an electric steel-manufacture furnace etc. especially in detail.

[0002]

[Description of the Prior Art] In arc furnaces including an electric steel-manufacture furnace, the artificial graphite electrode is used from the former. This graphite electrode is used under the very severe conditions influenced of scattering of a high current, high temperature, and melt etc. Especially, in the point of an electrode, the arc of a super-elevated temperature occurs, and an electrode will be exposed to a 400 degrees C - about 3,000 degrees C elevated temperature, and carries out oxidative consumption easily by the oxidizing gas which invaded from opening in a furnace etc. Since the rate that the cost of this electrode in a steel-manufacture furnace occupies is high, consumption of this electrode serves as big loss economically. 50 - 70 % of the weight produces the oxidative consumption of this electrode from a side face, and there is little consumption by the arc itself. Furthermore, since an electrode tapers off by oxidative consumption like a point, the oxidative consumption of a longitudinal direction is accelerated. Therefore, if antioxidizing from the side face of an electrode is enough, consumption of an electrode will decrease and an economical merit will be large.

[0003] For this reason, various proposals are made in order to prevent oxidation of an electrode. For example, there is a method of maintaining an electrode below to oxidation temperature by cooling by injection of the water to an electrode. However, when the moisture of a large quantity enters in a furnace, there is risk of a phreatic explosion, and since there is also little cooling effect of the whole electrode, this approach cannot expect sufficient antioxidizing effectiveness. Moreover, there is an approach which is going to form protective coating in an electrode and is going to protect an electrode surface. For example, the approach (JP,59-51499,A) of forming a non-conductive antioxidizing layer in a graphite-electrode front face and the approach (JP,3-45583,A) using the coating material which made the colloidal solution of a silica ultrafine particle distribute an alumina, a silica particle, etc. further are mentioned. However, since it is non-conductive, in order to secure the energization to an electrode, each of these conventional coating materials needs to avoid the chuck part of an electrode, and needs to perform coating. For this reason, there is a difficulty that antioxidizing in the problem or unsettled part on construction is not enough etc.

[0004]

[Problem(s) to be Solved by the Invention] The object of this invention is preventing the oxidative consumption of the graphite electrode used with an arc furnace. The more concrete object of this invention tends to solve the technical problem in the conventional antioxidizing material for graphite electrodes, and is offering the conductive antioxidizing material which coating to an electrode chuck part is also possible for, and was moreover excellent in the antioxidizing effectiveness in an elevated temperature especially on the occasion of coating construction.

[0005]

[Means for Solving the Problem] The conductive antioxidizing material of this invention is characterized by coming to contain the fireproof aggregate, a binder, carbon black, and a polymer emulsion. Hereafter, this invention is explained to a detail. First, as the fireproof aggregate in this invention, more than kinds, such as powder, such as silicide of nitrides, such as oxides, such as a silica, an alumina, a titania, and a zirconia, SiC, carbide of B₄C, CrC, WC, TiC, VC, ZrC, and NbC, and TiN, VN, NbN, ZrN, CrSi₂ and TiSi₂, and ZrSi₂ grade or silicon, are used. Moreover, metal powder, such as way ghost powder of ZrB₂, TiB₂, CrB, etc., and Fe, Co, nickel,

Cr, V, can also be used together with the desirable above-mentioned fireproof powder. Especially ZrB_2 and B_4C , TiC , SiC , and Si are suitable in respect of the stability between antioxidizing of carbon, and the heat of a paint film, and are used suitably.

[0006] Although it will not be especially restricted if the moderate paint film reinforcement after desiccation is obtained as a binder, inorganic system binders, such as various silicate, phosphate, and a nature binder of colloid, can be used suitably. For example, as a nature binder of colloid, colloidal silica, a colloidal alumina, a colloidal zirconia, etc. can use it suitably. Especially colloidal silica is the most desirable in respect of the water resisting property after desiccation, an adhesive property, stability, and a price. Furthermore, as carbon black, what is obtained by which processes, such as the furnace method, the acetylene method, thermal **, or the contacting method, can be used. For example, the graphitization carbon black which processed suitably 2000 degrees C or more of these carbon black at the temperature of 2500-3000 degrees C under the ambient atmosphere in which oxygen does not exist substantially (for example, inside of N_2 air current, a vacuum, or carbon powder) is used. That to which these graphitization carbon black has the value which ** (ed) thickness L_c of microcrystal (A) with particle diameter (nm) in the range of 1.0-3.0 suitably is used.

[0007] The 4th component in this invention is a polymer emulsion. As this polymer emulsion, a rubber latex and a resin emulsion are mentioned and there is an emulsion of the polymer obtained by the emulsion-polymerization method or an emulsion obtained by re-emulsification of a polymer. As a rubber latex, natural rubber latex or synthetic rubber latex is mentioned. As synthetic rubber latex, a butadiene polymer, a styrene-butadiene copolymer, an acrylonitrile-butadiene copolymer, a methyl-methacrylate-butadiene copolymer, an acrylate system latex, etc. are mentioned, for example. Moreover, as a resin emulsion, emulsions, such as polystyrene, a styrene acrylonitrile copolymer, a polyvinyl chloride, an ethylene-vinylacetate copolymer, a polymethyl methacrylate, and polyethylene, are mentioned. Of course, these can also use two or more kinds together. A styrene-butadiene copolymer latex, especially a carboxyl group content styrene-butadiene copolymer latex are suitably used among these polymer emulsions.

[0008] Although the loadings of the four above-mentioned indispensable components change with classes of the object and raw material etc. Generally solid content weight % in this 4 component whole quantity the fireproof aggregate 20 - 90wt%, Preferably a binder (solid content) 40 - 70wt% 2 - 30wt%, desirable -- 5 - 15wt% and carbon black -- 2 - 30wt% -- desirable -- a 10 - 20wt% and polymer emulsion (solid content) -- 0.05 - 10wt% -- it is preferably chosen out of about 0.05-3wt%. The stability of a paint film worsens between heat that the solid content of the fireproof aggregate is less than [20wt%], HAJIKE occurs, and it is easy to oxidize a base material. When the solid content of the fireproof aggregate exceeds 90wt(s)%, the refractoriness of a paint film becomes high too much, a base material is oxidized by the about 500-800-degree C low temperature range, and it stops moreover, functioning as a paint film in future temperature regions. Moreover, although few contents of binder solid content are so desirable that there are in respect of conductivity, they do not have adhesive strength as it is less than [2wt%], and tend to exfoliate. Moreover, if the content of binder solid content exceeds 30wt(s)%, although adhesive strength is excellent, it will produce a problem in respect of conductivity, and will cause a spark. Furthermore, although it is so desirable that many in respect of conductivity, when 30wt(s)% is exceeded, an antioxidizing slip is made to thicken, or the carbon black in a paint film burns between heat, and the content of carbon black reduces oxidation-resistant ability. Desired conductivity cannot be acquired although oxidation-resistant ability is excellent in the content of carbon black being less than [2wt%]. Furthermore, sliding-proof nature falls that the amount of a polymer emulsion (solid content) is less than [0.05wt%], if it exceeds 10%, it will pass, and it becomes imperfection in respect of the Tokiyasu quality.

[0009] Moreover, in this invention, components other than the above can be blended if needed. For example, graphite powder can be blended as an antioxidizing material component. Although an electrode new in the upper part is moved to a bond, an electrode holder (grasping machine) is moved to an electrode longitudinal direction and it reholds if an electrode is exhausted by operation of an arc furnace, a paint film and the electrode holder section may contact in this case, and a paint film may be damaged. When such, in order to prevent the breakage on the paint film at the time of contact (exfoliation), it is blending graphite powder into a paint film, and sliding-proof nature improves, and breakage on a paint film may be mitigated. 20-70wt% (preferably 40 - 60wt%) extent is added for graphite powder to the fireproof aggregate. in order [moreover,] to raise stability with the passage of time, an adhesive property, and conductivity -- water-soluble polymers, such as acrylic resin, -- 3 component whole quantity -- receiving -- about 0.01-3wt% -- it can also blend.

[0010] Combination of each of these components is usually performed as follows. The conductive antioxidizing

material of this invention adds water to the powder which mixed the above-mentioned component by the above-mentioned specific weight ratio, and is adjusted by performing mixing and equalization processing. Although a water addition changes with spreading gestalten, it is desirable to the solid content of a conductive antioxidizing material presentation component at sotogake, and is the most desirable. [25 - 100wt% of] [15 - 150wt% of] Mixed equalization processing of the above-mentioned presentation component is prepared by carrying out specified quantity addition of the above-mentioned mixed powder and the water, carrying out predetermined time mixing and performing equalization processing to the attritor equipment into which the alumina balls of for example, the mixed powder volume and this volume were put, and conductive antioxidizing material is obtained. There is especially no limit in mixing, an equalization processor, and an approach here, and mixed processing may be carried out by the usual desk mixer, the ball mill, a roll mill, etc. In addition, the object of said mixed equalization processing is for not making it depend on a paint film location for the presentation in the applied paint film, but making presentation distribution equalize. Thus, on the side face of the electrode for arc furnaces, the conductive antioxidizing material obtained can usually be applied to the thickness (after desiccation) of about 100-200 micrometers including a chuck part. spreading -- facing -- dip coating, brush coating, and a spray (fuel spray) - the approach that it is [from] most suitable among the general paint film formation approaches, such as law and electrostatic spray painting, can be chosen. Under the present circumstances, it is necessary to adjust conductive antioxidizing material to the activity viscosity suitable for each construction method.

[0011]

[Example] Hereafter, an example explains this invention to a detail further.

According to the example 1 and the combination presentation (solid content) of 2 following, two kinds of conductive antioxidizing material was obtained.

((I) Combination) (combination II)

** Titanium carbide powder 35wt(s)% 35wt%** graphite impalpable powder 25 ** 25 **** carbonization boron powder 10 ** 10 **** carbon black 15 ** 15 **** inorganic binder (colloidal silica) (solid content) 15 ** 15 **** dispersant (acrylic resin + surfactant) +0.5 ** +0.5 **** SBR latex +0.5 ** +3 ** -- here -- the carbon black of ** - trade name: Mitsubishi carbon black CF-9 (Mitsubishi Kasei Corp. make) -- using -- as ** dispersant Although acrylic resin and the mixture of a surfactant were used, said addition of ** and ** component is an addition to the total amount of aforementioned ** - ** component. That is, 80 weight sections addition of the water was carried out to the solid content 100 weight section of Combination I (example 1) or Combination II (example 2), respectively, it mixed with wet-grinding equipment "attritor" for about 24 hours, equalization processing was performed, and two kinds of conductive antioxidizing material was obtained.

[0012] <Volume resistivity> By the following approach, the result of having measured the volume resistivity value (ohm-cm) is shown in a table 1. The measurement result about the commercial antioxidizing material A is also shown collectively (example 1 of a comparison). In addition, the volume resistivity value measuring method is as follows. Beforehand, after performing coating processing for conductive antioxidizing material by predetermined thickness to the vertical side of the clear carbon plate (50x130x20mmt (t: thickness)) of resistance, it heated by the programming rate of 400 degrees C/H to it, and it held at predetermined temperature (under an atmospheric-air ambient atmosphere) for 1 hour, and the resistance test sample was obtained. This sample was inserted into the steel electrode of a resistance measuring device, and the volume resistivity of a paint film was computed by the following formula from the resistance pressurized and read with the total pressure of 1t using the AMUSURA pressurizer.

$$\text{Rho} = S/H \times (R - R_0)$$

rho: Volume resistivity of a paint film (ohm-cm)

S: The current passage cross section of a sample (cm²)

H: Sum total thickness of a coating layer (cm)

R: Total resistance after processing (omega)

R₀: Total resistance before processing (omega)

[0013]

[A table 1]

	体積固有抵抗 $\Omega \cdot \text{cm}$			
	熱処理条件			
	80℃×1H	300℃×1H	500℃×1H	800℃×1H
実施例1	<1	<1	<1	3
実施例2	<1	<1	<1	3
比較例1	28	102	102	絶縁化

[0014] <Sliding-proof trial> The result of having compared sliding-proof nature further about the antioxidizing material shown in Combination I (example 1) and II (example 2) is shown below. The antioxidizing material A of marketing for a comparison (example 1 of a comparison) was similarly processed to the carbon plate. The abrasion test equipment by Shinko Engineering Co., Ltd. was used for the sliding-proof testing device. After coating the above-mentioned conductive antioxidizing material so that about 200-micrometer thickness may be obtained after desiccation by the spray method, the carbon base material ($\phi 50 \times 8 \text{mm}$) top front face was made to season naturally it, and it was made into the test piece for assessment on it. This was set to the test board with a motor, it pushed against the steel ring (outer-diameter / bore = $\phi 43 / \phi 33 \text{mm}$) which was rotated by the per minute 50 revolution, cut the coating side with 10kg of loads on eight peripheries, and had a slot, the weight difference after 2000 revolutions was measured, and it considered as assessment of a sliding-proof property. A result is shown in a table 2.

[0015]

[A table 2]

	摩耗量 (mg)
実施例1	4
実施例2	1
比較例1	20

Thus, sliding-proof nature can be remarkably raised by making a latex contain in a coating layer, and since it starts at the time of migration of an electrode holder and grinds, a coating layer can be protected.

[0016] <Melting experiment by the raw material melting furnace> These antioxidizing material was applied to the thickness (after desiccation) of about 200-300 micrometers by brush painting on the graphite electrode ($\phi 155 \times 3750 \text{mm}$) front face used with a raw material melting furnace (4t), and the raw material melting experiment at a real furnace was conducted. The raw material used for melting was a magnesium oxide, and the time amount which melting took was about 3 hours and 30 minutes. The result of a melting experiment is shown in a table 3. For the comparison, the commercial antioxidant A (example 1 of a comparison) was written together. In the example 1 and the example 1 of a comparison, neither also produced troubles, such as a spark, but there was no problem on operation. In the example 1 of a comparison which applied the commercial item, to having exhausted 10.6% from the side face 8.6% from the electrode point, and there having been a total of 19.2% of weight reduction, the oxidative consumption from a side face decreased sharply, the oxidative consumption from a point also decreased simultaneously, and weight percentage reduction became below one half of the example of a comparison, and showed the good antioxidizing effectiveness by the examples 1 and 2 about the antioxidizing result.

[0017]

[A table 3]

	通電性	重量減少率 wt%	(内訳)	
			先端消耗	側面からの消耗
実施例1	良好	8.5	7.9%	0.6%
実施例2	良好	8.9	8.0%	0.9%
比較例1	良好	19.2	8.6%	10.6%

[0018]

[Effect of the Invention] According to this invention, spreading into an electrode chuck part is possible, and the conductive antioxidizing material which was excellent in sliding-proof nature and the antioxidizing effectiveness in an elevated temperature can be obtained.

.....
[Translation done.]